REMOTE SENSING OF CRITERIA AND NON-CRITERIA POLLUTANTS EMITTED IN THE EXHAUST OF ON-ROAD VEHICLES

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INTRODUCTION

Emissions from mobile sources are well known to play a central rolc in urban air pollution (photochemical smog formation, violation of CO and ozone O_3 standards, and aerosol formation). The Clean Air Act Amendments of 1990 call for auto makers to reduce tailpipe emissions of hydrocarbons and nitrogen oxides by 35 % and 60 % respectively. CO emission standards of no more than 10 g mi^{-1} for light duty motor vehicles have also been set. Additional emission reductions for all three pollutants have been scheduled for the early 2000s. Data collected from remote sensing studies of large fleets of in-use vehicles indicate that approximately half of CO, hydrocarbon (THC), and NO emissions are generated by less than 10% of vehicles. Moreover, remote sensing data suggest that fleet dynamometer testing significantly underestimates tailpipe emissions, and contribute to errors in model predictions (e.g., U.S. EPA's MOBILE4). A knowledge of the chemical composition of the exhaust plume emitted by on-road vehicles on a car-by-car basis therefore is essential when developing effective pollution abatement strategies, and in helping meet Clean Air Act objectives.

EXPERIMENTAL

A remote sensor incorporating UV-vis and IR spectrometers in conjunction with an innovative optical design has been developed. The instrument was used to non-invasively measure over 20 pollutants in the exhaust of 19 in-use vehicles powered by a range of fuels – reformulated Phase II gasoline, diesel, compressed natural gas, and methanol blended with 15% gasoline. CO_2, CO, aldehydes, aliphatic and speciated aromatic hydrocarbons were identified along with NO_x, determined as the sum of NO, NO_2; N_2O and HONO was also measured, although their levels were typically below the instrument's detection limit.

RESULTS AND DISCUSSION

The results are summarized in Table 1 below.

Table 1. Effect of fuel type on vehicle exhaust emissions.

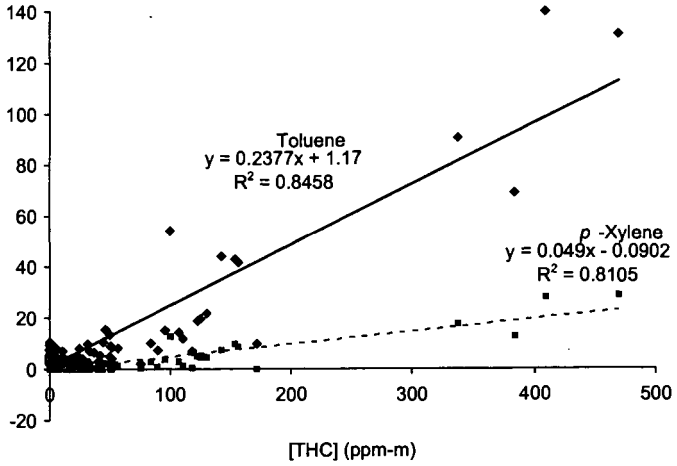
Fuel	$[HC]_{mean}$ (ppm)	$[CO]_{mean}$ (%)	$[NO]_{mean}$ (ppm)	$[NH_3]_{mean}$ (ppm)
Gasoline	126.5	1.92	475.6	317.0
Diesel	50.1	0	934.6	0.0
CNG	55.8	0.34	2041.3	12.1
M-85	25.5[§]	2.01	0.0	438.5

[§]Measured as methanol.

NH_3 levels in vehicle exhaust are reported for the first time on a car-by-car basis. The exhaust from gasoline- and methanol-powered cars was found to contain elevated levels of NH_3, in some cases over 1000 ppm, despite near stoichiometric air-to-fuel ratios, and were often significantly higher than corresponding NO levels. Catalyst efficiency is discussed as a function of NH_3 and NO concentrations in the exhaust of vehicles operating "cold" and "hot". In some of the tested vehicles, the three-way catalysts showed high reduction activity, but poor selectivity resulting in the formation of NH_3, and possibly other nitrogen-containing products other than N_2.

Remote sensing was also performed on the exhaust emissions from over 2,100 vehicles as they drove up a freeway on-ramp. Criteria pollutants, CO, THC, and NO, were found to follow a γ-distribution and agreed with data from previous remote sensing studies using a different technology; over half the total pollutant emissions are from 10 % of the fleet. Optical densities of the two principal aromatic hydrocarbon components of gasoline, toluene and xylene, were found to correlate well with THC measurements (Fig. 1), despite the fact that the measurements were made by different techniques; UV (aromatics) and IR (THC) absorption spectroscopy.

Figure 1.



Note: concentrations are shown as column densities, not as levels in undiluted exhaust.

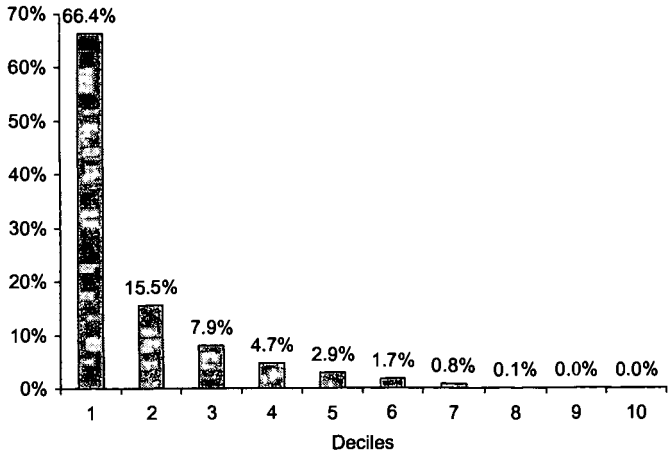
Emission rates of CO, THC, NO, toluene and xylene are shown in Table 2 below.

Table 2.

Pollutant X	Mean [X]/[CO_2]	Max. (ppm)	E_m (mg/km)
NO	0.00381	4963	940
NH_3	0.00056	3934	138
Toluene	0.00018	1620	44†
p-Xylene	0.000037	350	9†

†Based on relationship to THC emissions.

Figure 2.



SUMMARY AND CONCLUSIONS

For the first time, remote sensing was used to measure NH_3 directly in the exhaust plume emitted by on-road vehicles. It was shown that 66.4 % of the emitted NH_3 was produced by 10 % of the fleet as illustrated by the decile plot given in Figure 2; the first decile represents the fraction of the total analyte produced by the 10 % dirtiest fraction of the measured vehicle fleet, and so on.

Mean NH_3 emission rates were calculated at 138 mg km^{-1}, nearly twice as high as previous estimates. However, it is expected that NH_3 generation in three-way catalysts is highly dependent on driving conditions and, therefore, NH_3 emission rates will probably vary as a function of the remote sensing test site. These observations could have significant implications on the formation of ammonium nitrate aerosol and on the acid-neutralizing capacity of urban air masses and NH3 emissions from motor vehicles may need to addressed in future amendments of the Clean Air Act.

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The statement and conclusions in this paper are those of the contractor and not necessarily those of the Mobile Source Air Pollution Review Committee (MSRC) or the South Coast Air Quality Management District (SCAQMD). The mention of commercial products, their sources or their uses in connection with material reported herein is not to be construed as either an actual or implied endorsement of such products.